APPLICATION

FOR

UNITED STATES LETTERS PATENT

TITLE: **GAS SEPARATION APPARATUS AND GAS SEPARATION METHOD**

APPLICANTS: **Yoshinori TAJIMA and Takashi FUTATSUKI**

"EXPRESS MAIL" Mailing Label Number: EL890178085US
Date of Deposit: November 7, 2001

GAS SEPARATION APPARATUS AND GAS SEPARATION METHOD

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a gas separation apparatus and gas separation method for separating specific gases from a gas to be treated which contains a plurality of specific gases.

2. Description of the Related Art

Conventionally, various gases are used in a semiconductor manufacturing processes depending on the particular process adopted. For example, perfluoro compound (PFC) gas which is a mixture containing fluorine compounds such as CF_4, NF_3, C_2F_6, C_3F_8, SF_6, and CHF_3 is used as a reaction gas at the dry etching process or at the cleaning process for a thin film forming device. In these processes, a discharge gas is produced which contains the PFC gas.

Because these discharge gases such as PFC promote global warming and thus cannot be discharged out of the line without further processing, various methods are employed for treating these gases. The treating methods include (i) decomposition in which the PFC gas is decomposed by combustion, catalyst heating, or plasma decomposition; (ii) membrane separation in which these materials are separated by a membrane; (iii) distillation separation by subzero cooling in which the separation is achieved taking advantage

of the difference in the boiling points of the gases; and (iv) chromatographic separation in which separation is achieved by taking advantage of the difference in time for passing through a chromatographic column.

However, in the decomposition method (i), there are shortcomings in that a complete decomposition is difficult and the gas cannot be recovered for reuse because the gas is decomposed and discharged. In the membrane separation (ii), although nitrogen in the discharge gas can be removed, the separation between PFC gases is difficult. In the subzero cooling separation method (iii), separation between gases which only have a small difference in the boiling points, such, for example, as CF_4 and NF_3 with the difference being only 1 ℃, is difficult. In a conventional PFC recovery device employing the subzero cooling separation method, when recovering a mixture gas of CF_4 and NF_3, NF_3 must first be decomposed and the remaining CF_4 alone is then recovered. However, the trouble with this method is that NF_3 which is the most expensive gas among the PFC gases cannot be recovered. In the chromatographic separation (iv), there is a problem that when three or more PFC gases are present, these gases cannot simultaneously be separated and recovered.

SUMMARY OF THE INVENTION

The present invention has been conceived to overcome the shortcomings of the conventional gas treatment methods mentioned above, and one object of the present invention is to provide a gas

separation device and gas separation method capable of separating a mixture gas having a plurality of constituents, in particular, three or more constituents, inexpensively and with high purity.

According to the present invention, a mixture gas to be treated containing a plurality of gas constituents is first separated by distillation separation into a plurality of gas constituent groups, each of which group has similar boiling points, and then the specific gases within each of separated gas constituent groups are separated by chromatographic separation. In this manner, a mixture gas having a plurality of constituents, in particular, three constituents or more, can be separated inexpensively and with high purity.

For example, when a mixture gas having a plurality of gas constituents includes CF_4, NF_3, C_2F_6, and CHF_3, and nitrogen is an additional gas constituent, the gases can be separated by distillation separation into a first gas group which includes CF_4 (having a boiling point of −128 ℃) and NF_3 (having a boiling point of −128.8 ℃), a second gas group which includes C_2F_6 (having a boiling point of −78 ℃) and CHF_3 (having a boiling point of −82.2 ℃), and a third gas group which includes nitrogen (having a boiling point of −195 ℃). Then, by chromatographic separation, the mixture gas of the first gas group can be separated into CF_4 and NF_3. The mixture gas of the second gas group can similarly be separated by chromatographic separation into C_2F_6 and CHF_3. the separated gases of CF_4, NF_3, C_2F_6, and CHF_3 can respectively be recovered for reuse.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a block diagram showing the structure of a device according to the present invention.

Fig. 2 is a diagram showing the structure of a chromatographic separator according to the present invention.

DESCRIPTION OF PREFERRED EMBODIMENT

In the present invention, the plurality of specific gases are, for example, PFC gases discharged from a semiconductor manufacturing process. The PFC gases include any one of a fluorine compounds having at least one of the elements C, N, and S as the constituting element. Specifically, examples of PFC gases include CF_4, NF_3, C_2F_6, C_3F_8, SF_6, and CHF_3. The present invention is particularly effective when the PFC gases include at least the following three constituents: CF_4, NF_3, and C_2F_6 or CHF_3 or when the PFC gases include at least the following three constituents: C_2F_6, CHF_3, and CF_4 or NF_3. The present invention is especially effective for separation of PFC gases containing both CF_4 and NF_3 which have similar boiling points or for separation of PFC gases containing both C_2F_6 and CHF_3 which have somewhat similar boiling points. The gas to be treated usually contains 0.1 % to several percent PFC gas and nitrogen as the remainder gas.

The gas to be treated is first introduced to a distillation separator 10 for separating the gases by distillation separation into a plurality of gas constituent groups each of which group has

similar boiling points. As the distillation separator 10, any known device which uses a distillation column can be used. That is, in the distillation column, gas constituents included in the gas to be treaded are cooled to respective boiling points and liquefied to form a gas-liquid state so that separation and purification can be performed. For example, a mixture gas of two constituents having similar boiling points can be grouped as one group, and PFC gases can be separated and purified into a plurality of groups. More specifically, the gas to be treated is distillation separated into three gas groups, that is, CF_4 and NF_3 each of which has a boiling point near -128 ℃ constituting a first group, C_2F_6 and CHF_3 which have boiling points of -78 ℃ and -82.2 ℃, respectively, constituting a second group, and nitrogen having a boiling point of -195 ℃ constituting a third group. The separated first gas group and second gas group are then each chromatographically separated into high purity specific gases by a chromatographic separators 12a and 12b provided downstream of the distillation separator. Nitrogen in the third gas group is recovered and reused. In the distillation separator 10, it is possible to further obtain fourth, fifth, etc. gas groups depending on the composition of gas constituents in the mixture gas to be treated.

The first and second gas groups separated at the distillation separator 10 are then respectively introduced to a chromatographic separators 12a and 12b for separating the specific gases

constituting each gas group and having similar boiling points, by chromatographic separation. That is, in the first group, a first specific gas (e.g. CF_4) and a second specific gas (e.g. NF_3) are separated and in the second gas group, a third specific gas (e.g. C_2F_6) and fourth specific gas (e.g. CHF_3) are separated. Because the chromatographic separation operation is similar for both gas groups, the chromatographic separation operation will be described below for separation of CF_4 and NF_3 in the first gas group.

As the chromatographic separators 12a and 12b, any known chromatographic separator having a column filled with a given filler can be used. The first gas group is passed through the separator 12a. In this manner, this first gas group is separated into its constituents because the constituents have different retention times due to difference in the affinity of the gas constituents with respect to the filler. As a filler, for example, silica gel or molecular sieve can be used for separating CF_4 and NF_3. In the chromatographic separators 12a and 12b, nitrogen is used as a carrier gas and CF_4 and NF_3 are separated by sequentially desorbing and discharging CF_4 these gas constituents adsorbing onto the filler.

When a mixture gas fraction having both CF_4 and NF_3 is obtained from the separator 12a, it is preferable to return this fraction to the inlet side. For example, while passing the carrier gas, which is the nitrogen gas, a predetermined amount of mixture gas fraction can be mixed into the nitrogen gas, and a fraction containing CF_4

and a fraction containing NF_3 can be separately collected.

It is also preferable to provide a plurality of columns in the chromatographic separator 12a (or 12b) to form a simulated-moving fed type chromatographic separator in which the first gas group is supplied to each column in sequence and each fraction is collected from each column in sequence. Fig. 2 shows a configuration example of a simulated-moving fed type chromatographic separator 1 in which four columns 1a, 1b, 1c, and 1d are provided, and fractions are obtained by supplying the first gas group to the columns in sequence. For example, nitrogen can be continuously supplied to the columns 1a, 1b, 1c, and 1d as a carrier gas, and the first gas group can be introduced to the columns in sequence by switching, in sequence, the feed gas inlet valve in the downstream direction. Because gas of nitrogen, gas of CF_4 and nitrogen, gas of CF_4, NF_3 and nitrogen, and gas of NF_3 and nitrogen flow out from each of the columns 1a, 1b, 1c, and 1d, in that order, the gases can be separated and discharged by switching a valve at the exit side in sequence and driving corresponding one of vacuum pumps 2a, 2b, 2c, and 2d. The mixture fraction containing both CF_4 and NF_3 is circulated to and joined with the feed first gas group. In this manner, gas of nitrogen, gas of CF_4 and nitrogen, and gas of NF_3 and nitrogen are obtained at the exit of the chromatographic separator.

It is preferable to perform collection of the gas for each constituent at the exit of the chromatographic separator and the

switching of the valves in a simulated-moving fed type chromatographic separator 1 in Fig. 2 based on control conditions which are set based on the gas composition of the first gas group or the performance of the filler, or an analysis result of the gas at the exit. When the gas collection and valve switching are performed based on the analysis result of the gas at the exit, gas constituents can be detected using, for example, a differential thermal detector (TCD) or Fourier transform-infrared analyzer (FT-IR), and the control can be performed based on the analysis. With this process, the gas is separated into its constituents, and thus, in the fractions for CF_4 and nitrogen, and for NF_3 and nitrogen, a pure mixture can be obtained with almost no other materials present.

The obtained fraction of CF_4 and nitrogen and the obtained fraction of NF_3 and nitrogen are supplied to concentrators as necessary. As the concentrator, it is preferable to use a membrane separator or a subzero cooling device. In particular, by circulating the concentrated gas several times in a membrane separator or by using a multiple-step membrane separator, almost 100% of nitrogen can be separated, leaving a pure, 100% concentration of CF_4 gas and NF_3 gas. The CF_4 gas and NF_3 gas can then be recovered and reused, for example, at the dry etching process or cleaning process of a thin film forming device in the semiconductor manufacturing process.

The above chromatographic separation by the chromatographic

separator and concentration by concentrator which is optional treatment means are also similarly performed on the second gas group. In this manner, pure, 100% concentration of C_2F_6 gas and CHF_3 gas can be obtained. Similar to the gases in the first gas group, C_2F_6 gas and CHF_3 gas can be recovered and reused, for example, at the dry etching process or cleaning process of a thin film forming device in the semiconductor manufacturing process.

In the embodiment, by performing the upstream distillation separation, the gas to be treated which contains, for example, four specific gases CF_4, NF_3, C_2F_6, and CHF_3, and another gas, nitrogen, can be separated into three gas groups having different boiling points. Among the three gas groups, each of two gas groups is a mixture gas of two gas constituents. Thus, by further using chromatographic separators, CF_4 and NF_3, and C_2F_6 and CHF_3, which are each difficult to be separated by other separation methods, can reliably be separated. The separated gases of CF_4, NF_3, C_2F_6, and CHF_3 can then be recovered and reused.

As another embodiment, in a case where the gas to be treated contains three specific gases, CF_4, NF_3, and C_2F_6 or CHF_3, and another gas, nitrogen, by performing the upstream distillation separation, the gas to be treated can be separated into three gas groups with different boiling points, the first gas group including CF_4 and NF_3, the second group including C_2F_6 or CHF_3, and the third group including nitrogen. Among the three gas groups, the mixture gas of CF_4 and NF_3 can be separated into CF_4 and NF_3 using a chromatographic

separator for separating the specific gases. When the gas to be treated contains three specific gases, C_2F_6, CHF_3, and CF_4 or NF_3, and another gas, nitrogen, by performing the upstream distillation separation, the gas to be treated can be separated into three gas groups with different boiling points, the first gas group including C_2F_6 and CHF_3, the second gas group including CF_4 or NF_3, and the third gas group including nitrogen. Among the three gas groups, the mixture gas of C_2F_6 and CHF_3 can be separated into C_2F_6 and CHF_3 by further using a chromatographic separator for separating the specific gases.

Other examples of PFC gases include C_3F_8 and SF_6, in addition to CF_4, NF_3, C_2F_6, and CHF_3. The former PFC gases can be separated relatively easily by various means. For example, C_3F_8 (having a boiling point of -36.7 ℃) can be separated in the above example as a fourth gas group in the distillation separator. SF_6 (having a sublimation temperature of -63.8 ℃ and melting point of -50.8 ℃) obtained in the chromatographic separators 12a and 12b as a fraction that is further apart. Thus, fractions containing SF_6 can be separated from the fraction that is separated as nitrogen in the above example.

Also, nitrogen is obtained at the distillation separator, chromatographic separator, and concentrators. Nitrogen, on the other hand, is necessary as a diluting gas introduced before a vacuum pump in order to dilute hydrogen fluoride in the discharge gas from the semiconductor manufacturing process, and as the carrier gas

for the chromatographic separator. It is therefore preferable to reuse the obtained nitrogen.

It is highly probable that the nitrogen gas to be reused contains very small amounts of PFC gases. Therefore, it is preferable to treat the nitrogen gas to remove the very small amounts of PFC gases within the nitrogen gas to be reused. As the process, it is preferable to employ a known method for decomposing the PFC gases, such as, for example, plasma decomposition process, combustion, and catalyst heating process, or to repeat the distillation separation and chromatographic separation, to separate the PFC gases and increase the purity of nitrogen.

Example 1

As a sample discharge gas, nitrogen gas was prepared which contained 1% each of CF_4, NF_3, C_2F_6, and CHF_3 (volume percent). The sample discharge gas was introduced to a known distillation column where distillation operation was performed to separate the discharge gas into a first gas group containing CF_4 and NF_3, second gas group containing C_2F_6 and CHF_3, and third gas group containing nitrogen. The concentration of CF_4 in the first gas group was 50%, the concentration of NF_3 in the first gas group was 50%, the concentration of C_2F_6 in the second gas group was 50%, and the concentration of CHF_3 in the second gas group was 50%.

The first gas group was passed through a chromatographic separator which uses a column filled with silica gel and nitrogen as the carrier gas. As a result, gas of CF_4 and gas of NF_3 were

separated and discharged in that order at the separator column exit, due to the difference in the retention times. The purity of each gas was 100%.

Similarly, the second gas group was passed through a chromatographic separator which uses a column filled with silica gel and nitrogen as the carrier gas. As a result, gas of C_2F_6 and gas of CHF_3 were separated and discharged in that order at the separator column exit, due to the difference in the retention times. The purity of each gas was 100%.

An analysis of nitrogen obtained at the distillation separator 10 and chromatographic separators 12a and 12b indicated that the nitrogen gas contained 10 ppm of PFC gas. The PFC gas was decomposed to a concentration of 0 ppm and neutralized by applying a plasma decomposition process to the obtained nitrogen. It was thus confirmed that the obtained nitrogen gas is usable as a diluting gas before the vacuum pump for diluting hydrogen fluoride within the discharge gas of the semiconductor manufacturing plant or as a carrier gas for the chromatographic separator.

According to the embodiment, by performing the upstream distillation separation, the gas to be treated which contains a plurality of specific gases and nitrogen as another gas can be separated into at least three gas groups with different boiling points, including at least one group containing two gas constituents of which the boiling points are similar. Using the chromatographic separation for separating specific gas, the plurality of mixture

gases can then be reliably separated into each constituent, the constituents being difficult to be separated by other methods, such as, for example, CF_4 and NF_3, and C_2F_6 and CHF_3. In other words, according to the present invention, a plurality of constituents, in particular, three or more PFC gas constituents, that cannot be separated by a single separation method such as distillation separation or chromatographic separation, can be separated inexpensively and in high purity. The separated CF_4, NF_3, C_2F_6, and CHF_3 can be recovered and reused.